TORREFACTION PROCESS: THE EFFECT OF TEMPERATURE AND RESIDENCE TIME TO THE PRODUCTION OF TORREFIED RUBBERWOOD

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (BKC)

Faculty of Chemical & Natural Resources Engineering
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JANUARY 2014

ABSTRACT

This thesis presents the study on the effect of temperature and residence time towards the torrefied rubberwood fibre characteristics. In order to produce the biomass product from the rubberwood fibre (RWF), torrefaction process of the sample remove the moisture and oxygen content inside by applying the process with the temperature in range between 200-300 °C (Stelt et.tal., 2008). The torrefaction process might change the morphology structure, decomposition pattern, wavelength spectrum and most importantly its energy value. This research is important in studying the effect of the temperature and residence time during the torrefaction process on the characteristics of the rubberwood fibre. In this research, the temperature applied for the torrefaction was 180 °C, 250 °C and 320 °C to investigate the effect of temperature towards the product. The heating rate use was 10°C/min and the nitrogen gas was flush throughout the tubular glass reactor for 15min before the process. Holding time in the process also being manipulated at each temperature used by 10, 20 and 30min. The characteristic data of rubberwood fibre(RWF) after torrefaction was collected and compared by using fourier transforms infrared spectroscopy (FTIR) to define wavelength, scanning electron microscope (SEM) to get the surface morphology of the product, thermal gravimetric analysis (TGA) to recognize materials characterization through analysis of characteristic decomposition patterns, and lastly the most important is bomb calorimeter to measure the energy value for the combustion. SEM structure at 3K X magnificent, the structure of the torrefied product at 320°C shows significant difference compared to the others. In contrast, the structure of the other two torrefieds product at different temperature and constant residence time shows no major change. The result then compared with FTIR analysis at which it shows loss of functional group represent the RFW component especially hemicellulose for torrefied RWF at 320°C. Based on the energy value of the product, it can be concluded that the higher the temperature of torrefaction, the higher the energy value of the product. The graph of percentage of weight versus temperature from TGA concludes that the torrefied RWF at higher temperature takes longer time to decompose.

Keywords: Biomass; rubberwood fibre (RWF); torrefaction; characteristics

ABSTRAK

Kertas kajian ini berkisar mengenai kesan suhu dan masa ke atas ciri-ciri gentian kayu getah yang menjalani proses torrefaction . Untuk menghasilkan produk biomas daripada serat kayu getah (RWF), proses torrefaction menyingkirkan kandungan kelembapan dan oksigen di dalam sampel dengan menggunakan proses dengan suhu dalam julat antara 200-300 ° C (Stelt et.tal . , 2008). Proses torrefaction akan mengubah struktur morfologi , corak penguraian, spektrum gelombang dan nilai tenaga. Kajian ini penting dalam mengkaji kesan suhu dan masa semasa proses torrefaction pada ciri-ciri gentian kayu getah . Dalam kajian ini , suhu yang digunakan untuk proses torrefaction adalah 180 ° C , 250 ° C dan 320 ° C. Penggunaan kadar pemanasan adalah 10 ° C / min dan gas nitrogen dilalukan ke dalam reaktor kaca berbentuk tiub untuk 15min sebelum proses. Masa ketika proses juga dimanipulasi pada setiap suhu yang digunakan iaitu pada 10, 20 dan 30 minit. Data ciri fiber kayu getah (RWF) selepas torrefaction dikumpulkan dan dibandingkan dengan menggunakan Fourier pengubah spektroskopi inframerah (FTIR) untuk menentukan panjang gelombang , pengimbas mikroskop elektron (SEM) untuk mendapatkan morfologi permukaan produk, analisis gravimetrik terma (TGA) untuk mengenali bahan-bahan pencirian melalui analisis corak penguraian ciri, dan akhir sekali yang paling penting ialah kalorimeter bom untuk mengukur nilai tenaga untuk pembakaran. Struktur SEM untuk 3K X pembesaran , struktur produk torrefied pada 320 ° C menunjukkan perbezaan yang signifikan berbanding dengan yang lain . Sebaliknya, struktur dua produk lain pada suhu yang berbeza dan masa tinggal yang tetap tidak menunjukkan perubahan besar . Hasilnya kemudian dibandingkan dengan analisis FTIR di mana ia menunjukkan kehilangan kumpulan berfungsi mewakili komponen RFW terutama hemiselulosa untuk produk RWF pada 320 ° C. Bagi nilai tenaga produk, kesimpulan boleh dibuat bahawa lebih tinggi suhu torrefaction , semakin tinggi nilai tenaga produk. Daripada graf % berat berlawanan suhu dari TGA, dapat disimpulkan bahawa produk RWF yang melalui proses torrefaction pada suhu yang lebih tinggi mengambil masa yang lebih lama untuk mereput.

Keywords: Biomass ; fiber kayu getah (RWF); torrefaction ; ciri-ciri

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LIST OF ABBREVIATIONS

Hg	heat of combustion
m	mass
qrxn	heat of reaction
ΔUrxn	internal energy changes
ΔU$_{CAL}$	internal energy for process
Δ U$_{HEATING}$	internal energy of heating
VVM	volume per unit volume

Greek

e	constant for fuse wire

Subscripts

g	gas
l	liquid

LIST OF ABBREVIATIONS

RWF	Rubberwood fibre
FTIR	Fourier transforms infrared spectroscopy
TGA	Thermo Gravimetric Analysis
SEM	Scanning electron microscope
ISO	International Standard Organization

1 INTRODUCTION

1.1 Motivation and statement of problem

Energy plays major role to human because it is use in daily activities, transportation and so on. The importance of energy can be proven due to the attention of politicians, policy makers, researchers and businessman towards this area. Long terms warning took on a prophetic aspect as fuel shortages and rising costs nearly paralyzed the industrial economies and literally shocked the world into an inflationary period that is not yet ended (Nagarajan and Sai, 1995). This problem then create the awareness of renewable energy as an important source as a backup for the existence of natural energy resources that may depleted each day and will not applicable to such a certain condition due to the changes of environment. The world may change into a new generation which the new product will replace the old one as the requirement for the suitability of the design following the power of the new energy sources. Transportation as the example, the design of the car might change drastically as the renewable energy that will replace fuel may not give a great combustion but with the design of the aerodynamic and so on, it might give a better results. Furthermore, the renewable energy is believed to grow fast following the nowadays situation.

There are few types of renewable energy resources that can be used such as solar, wind, hydroelectric, geothermal and biomass. Thousands of years before, mankind realize that the energy can be created by this sources but its only be used as personal use in a small scale. As the years increased, the human invention and technology became more complicated and growing well. The devastation of oil crises on year 1973 triggered the attention of the world to the renewable energy as the new sources to be added to the solution towards the depletion of non-renewable energy sources. The research towards a better performance of this solar, wind, hydroelectric, geothermal, biomass and others renewable energy greatly arise then in order to continue the efficient world life as a human kind that obviously will be effected by sudden depletion of non-renewable energy as all field, economic, industrial, daily activities, all could be change to the worse. All type renewable energy has a different approach to be converted into useful energy. Solar energy, for example come in form of heat and radiant light from the sun,

and been harnessed by using the solar panel. Wind energy is converted into a useful form of energy, such as using turbines to generate electrical, pumps for drainage, mechanical power from windmills, or sails as the ships need it. Electricity also can be generated by hydropower by the gravitational force of flowing water or falling of water in damping system. For geothermal energy, the temperature differences between surfaces and core of earth results in the conduction of thermal energy that continuously been produced in the heat form. However, compare to the other alternative energy resources, biomass benefits applicable in almost of the climate in different country make it has greater potential, since it is renewable, in contrast to the nature of the fossil fuels (Natarajan et al., 1998).

Biomass is seen as one of the best options that can provide a renewable fuel which can be utilized in a range of energy conversion technologies (Farah, 2008). It being used for energy purposes is derived from a number of sources. Residues from forests, wood processing, and food crops dominate. According to Chum et al. (2012), short-rotation energy crops, grown on agricultural land specifically for energy purposes, currently provide about 3–4% of the total biomass resource consumed annually. The total area of land used for bioenergy crops is difficult to quantify accurately because of large data gaps. Furthermore, some energy crops are grown for competing non-energy uses. During photosynthesis, the process need carbon dioxide (CO_2) as a requirement and naturally the CO_2 cycle process could be obtain from biomass process make the surrounding ecosystem became more efficient. This is because biomass release energy in the form of heat when it is burned and the carbon element reacts with oxygen in the air to produce carbon dioxide. The combusted amount of carbon dioxide obtain from the process could be equal to the amount which was extracted from the air when the plant was growing up in is full combustion process of biomass. The only sustainable carbon carrier out of others renewable energy makes more people put an attention on biomass. Animated from organic matter, biomass comes from not only organic wastes, such as solid waste, sewage and pulp derived black liquor but also crops and forestry. Well development of industrial activity of furniture production and forestry has made woody biomass being used widely compared to other various kinds of biomass as the source of energy for such a long time of period before. Compare to food crops, woody material could generate more profit as it production per size of the land is more than food crops production per size of the land. This is because, the woody material given in bigger size

compare to food crops and producing a bigger yield. Less amount of fertilizer also needed by woody material and contain higher energy compare to food crop. Fact that fossil fuels cannot be renewable, limits in quantity and always increasing in cost due to world economic driving the demand for this alternative energy sources and made the industrial realized the potential of the woody biomass in the future.

In Malaysia, there are potential option of the woody biomass made out from the raw waste material that is basically come from one of the economic sources for the country such as oil palm and rubber. Comprising 12 of the 14 states in the Malaysian federation, the Peninsular Malaysia is among the world's most important rubber growing area. Rubber is also plant in Sabah and Sarawak and altogether Malaysia produces almost 20% of the world's natural rubber. More than half of Malaysia's rubber comes from thousands of privately owned small landholdings and the rest is grown on big estates owned by various companies each can cover over a thousand hectares. Malaysia in total has 1.7 million hectares of rubber plantation (Alves and Figuereido, 1989). Annual rubber seed production in Malaysia that is high makes the source unlimited and renewable throughout the years. This research using rubber wood as the sources of energy then might be important in providing the continuity that benefit the country not only in term of its application but also economy. Unfortunately, being advantage with the continuity production of the rubber wood, it also had the disadvantages at which the moisture content in the rubber wood itself that would make it less efficient as biomass for energy application. The other disadvantages of the woody biomass are higher oxygen content, low calorific value and also hydrophilic nature. In addition, it also has heterogeneous composition and tenacious fibre structure which make the process more complicated. The solution come towards the moisture problem is the implementation of torrefaction process to improve the woody biomass property.

Torrefaction is a process which removes the moisture inside the sample and act as an important thermal treatment of energy generation in the modification of biomass. It is important to removes the moisture in the sample as it will increase calorific value and the efficiency of the combustion process. The process typically involves slow heating in the temperature range of 200-300 C (Stelt et al., 2008). This process also eliminates moisture and carbon dioxide, acted as the agent removal of oxygen from the biomass then resulting in a lower O/C ratio of fuel, depolymerizes the long polysaccharide

chains, and producing a solid product with an increased energy density on a mass basis (Prins et al., 2006). After the torrefaction process been implemented, the heat supply on the process will dry the sample and automatically the initial weight of the sample will decrease as affect in loss of moisture and its component constituents.

Rubberwood component consist of lignin, hemicellulose and cellulose which will differ in their percentage as the pre-treatment is going according to the temperature and residence time. Usually wood contains about 50% cellulose (Sullivan, 1955) up to 35% hemicelluloses (Xu et al., 2010) and have between 18-25% lignin (Capanema et al, 2005). Apart from that, hemicellulose undergoes the most pronounced decomposition reactions during the torrefaction process (Bridgeman et al., 2008)

1.2 Objectives

The objectives of this research is to study the effect of the temperature and residence time towards the characteristics of torrefied rubberwood.

1.3 Scope of this research

At first to produce an efficient energy application by using rubber wood biomass, it is necessary to find a common sample of rubber wood fibre (RWF) as the raw material. The sample may have high value of moisture because of exposure. Torrefaction process will be used as pre-treatment to remove the moisture in the sample with temperature of 180 °C, 250 °C and 320 °C as the manipulated parameter. Characteristic of RWF after torrefaction will be describe by using Fourier transforms infrared spectroscopy (FTIR) to obtain an infrared spectrum, Scanning electron microscope (SEM) to get the image of the sample, moisture analysis to measure the moisture content , thermal gravimetric analysis (TGA) to recognize materials characterization through analysis of characteristic decomposition patterns, and lastly bomb calorimeter to measure the calorific value which will determine the verification of the energy. After being weighted, the process will be continue by the torrefaction of the sample based on different temperature that being mention before. The product sample characterization analysis then will be carried out to measure changes and differences between each product.

1.4 Main contribution of this work

As the objective of the research is to investigate temperature and residence time as the manipulated variable on the production of the torrefied rubberwood fibre, it is believed that the results from this research can show the energy contain from the torrefied rubberwood fibre in a small scale. The energy and calorific value resulting from this research will show the real potential of the rubberwood sawdust to be implemented as one of the most important biomass in Malaysia.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the statistics related to the research, previous study and general design of temperature profile.

Chapter 3 gives a review of the process methodology including equipment and main procedure of the process.

Chapter 4 is devoted to the result of the torrefaction process and characteristic analysis, it then being discussed and related with previous study.

Chapter 5 gives the conclusion and recommendation on this research and relation to the industries.

Chapter 6 gives the references on the citation given on literature review and result discussion.

2 LITERATURE REVIEW

2.1 Overview

In this chapter, an introductory remarks towards the significant of rubberwood material to be converted to valueable products will be discussed. The statistics and citation shown also will concrete the fact that being stated in this chapter. The characteristics of sample and previous study also were described in detail on this chapter.

2.2 World Energy Consumption

2.2.1 Non-renewable energy

Depletion of non-renewable energy made the world currently increase the effort to challenges and reduce the dependence on non-renewable energy especially fossil fuels to sustain the world energy that is really important in human life. Renewable energies now became really important sources to replace the non-renewable sources. Furthermore, as mention by Nagarajan and Sai (1995) the fuel shortages and rising costs almost paralyzed the industrial economies and literally shocked the world into an inflationary period that is not yet ended.

According to the International Energy Agency's findings published in June 2006, world production of liquid fuels is expected to reach the peak at around 2014. For natural gas, peak production is anticipated at around 2030. The overall resource will then be in declining pattern and by 2030 the demand will exceed production by 18%. Therefore, sustainability in fossil fuels will be an issue in the long term. On the other hand, renewable sources provide a healthy prospect for sustainability because they are resources that are almost unaffected although used continuously and in large volumes. For the future, this is why more research needs to be done in order to enhance and develop the quality and quantity of the renewable energy.

2.2.2 Renewable energy

Voronkin et tal (1995) stated that in terms of level of development, nontraditional renewable sources of energy may be divided into four types which is the energy sources that are highly developed and possess stable technical and economic indicators (hydro-power, wood fuel) as the first type. The second type energy sources that are not very widely used (geothermal energy, wind energy) the technical and economic indicators of these types of energy sources depend strongly on local conditions and their domain of application is limited by their energy potential. The third type of energy sources is energy that are currently being developed and which show great potential, if their technical and economic indicators are improved (solar energy, biomass-generated energy, the use of low-potential heat by means of heat pumps). The last type of energy sources is energy that are currently at the stage of hypothetical development (all forms of energy derived from the oceans and the heat from dry Earth rocks). Evaluations of the efficiency gained from application of these types of energy sources have yet to be subjected to sufficient investigation. From all type of energy mention by Voronkin et tal (1995), solar energy, hydroelectric energy, wind energy, geothermal energy and biomass energy is the famous sources of renewable energy that will be discussed and compared to the extent of the best future renewable energy sources.

2.2.2.1 Solar energy

Solar energy is the energy which can be generated from the sun and generated into electricity in order to fulfill daily activities. In order to generate the electricity directly from the sunlight, there are two principal ways which are solar thermal electricity and solar PV cells. Solar thermal is form of active solar heating where the sun is gives out energy and was collected using either flat-plate or evacuated tube collectors and usually used for domestic hot water or swimming pool heating. Solar thermal electricity concentrates the sunlight using a system of collectors and then water was heats to sufficiently high temperatures to turn a steam turbine and hence generate electricity. According to International Energy Agencies (2012), the market for concentrating solar thermal power (CSP) continued to develop in 2012, with total global capacity up more than 60% to about 2,550 MW. Spain accounting for most of the 970 MW brought into operation as the market doubled over year 2011. From the period time of 2007 until 2012, total global capacity grew at an average annual rate approaching 43%. By adding 950 MW to increase operating capacity by 95% to a total of 1,950 MW, Spain continues

to dominate the world for the deployment and total capacity of CSP technology. The world's first hybrid CSP-biomass and the world's first commercial Fresnel plant were built on 2012 completing the technology development in 2012.

Solar PV cells emits electrons by its special surface that when exposed to light. DC current that produce from moving electrons passed through an inverter to produce alternating current. The solar photovoltaic (PV) market shows a good market development with total global operating capacity reaching the 100 GW milestones in 2012. By comparing with year 2011, the market was less capacity operation carried out but likely higher in shipment levels, and the more than 29.4 GW added represented nearly one-third of total global capacity in operation at end of the year. The thin film market share fell from 15% in 2011 to 13% in 2012. Eight countries added more than 1 GW of solar PV to their grids in 2012, and the distribution of new installations continued to broaden. By year's end, eight countries in Europe, three in Asia, the United States, and Australia had at least 1 GW of total capacity. The leaders for solar PV per inhabitant were Germany, Italy, Belgium, the Czech Republic, Greece, and Australia.

2.2.2.2 Wind energy

Wind energy is the other form of common energy used in suitable climate country either for a large scale wind farms for country electrical sources as well as in small individual turbines for providing electricity to rural residences area. Wind power is the conversion of wind energy into kinetic energy and then electricity by using wind turbines. Electrical generator is used to convert wind power the rotation of turbine blades into electrical current. International Energy Agencies (2012) reported that during 2012, almost 45 GW of wind power capacity starts operation with increasing global wind capacity 19% to almost 283 GW. Capacity on 2012 is increasing at which around 44 countries added capacity and at least 64 had more than 10 MW of reported capacity at the end of the year, and 24 had more than 1 GW in operation. From the end period of 2007 until 2012, the annual growth rates of cumulative wind power capacity was averaged by 25%. The global market in 2012 was dominates by the United States and China at nearly 60% of the total followed by Germany, India, and the United Kingdom at far behind. Others in the top 10 for the operation capacity added were Italy, Spain, Brazil, Canada and Romania. However year 2012 represented about 27% of the world

market and accounted for just over 37% of total global capacity fall in percentage from 40% in year 2011.

2.2.2.3 Geothermal energy

The geothermal energy is from thermal energy generated and stored in the Earth. Thermal energy is the energy that determines the temperature of matter. According to Schubert (2012), earth's 20% of geothermal energy originates from the original sources of the planet and 80% from radioactive decay of minerals. The difference in temperature between the core of the planet and its surface drives continuous thermal energy conduction in the form of heat from the depth to the upper surface. The basic system comprises drilling a deep injection well and a production well within the same hot fractured rock mass. Water is forced down the injection well, passing through the hot fractured rock mass to pick up heat and then returning up to the surface via the production well. This hot water is then used to produce steam or another more volatile gas to drive turbines to produce electricity (Sanyal et al., 2007). According to International Energy Agencies (2012) geothermal resources provide energy in the form of direct heat and electricity, totaling an estimated 805 PJ (223 TWh) in 2012. On the divisions of the energy, two-thirds of this output was delivered as direct heat, and the remaining was generated as electricity. During 2012, the geothermal direct which refers to direct thermal extraction for heating and cooling uses continued to increase globally. The technology involved for direct use is the application of ground-source heat pumps (GHP), which use electricity to extract several units of thermal energy from the ground for every unit of electrical energy spent. Output is known to have grown by an average of 10% annually from period 2005 until 2010 although there are limited data available on recent growth in direct use of geothermal energy. In year 2012 there are at least 78 countries using the direct geothermal heating process. Largest amounts of geothermal heating capacity was hold by the China, United States, Sweden, Germany, and Japan having together for about two-thirds of total global capacity. China remains the leader in direct geothermal energy capacity used per year (21 TWh in 2010), followed by the United States (18.8 TWh in 2012), Sweden (13.8 TWh in 2010), Turkey (10.2 TWh in 2010), Iceland (7.2 TWh in 2012), and Japan (7.1 TWh in 2010). For average annual geothermal energy use per person, Iceland, Sweden, Norway, New Zealand, and Denmark lead the percentage of the capacity.

2.2.2.4 Hydroelectric energy

Hydroelectricity is a form of electric which produce through the use of the gravitational force of falling or flowing water. Hydroelectric plants can be easily regulated to follow variations in power demand. Unlike fossil-fuelled combustion turbines, construction of a hydroelectric plant requires a long lead-time for site studies, hydrological studies, and environmental impact assessment. International Energy Agencies (2012) reported that hydrological data up to 50 years or more is needed to select the best sites and operating system for a large hydroelectric plant. Approximately 30 GW of new hydropower capacity was added in 2012 which increasing the global capacity by about 3% to an estimated 990 GW. China, Brazil, the United States, Canada, and Russia, which together account for 52% of total installed capacity are the top countries for hydro capacity out of total capacity. In year 2012, hydropower generated an estimated 3,700 TWh of electricity, including approximately 864 TWh in China, followed by Brazil (441 TWh), Canada (376 TWh), the United States (277 TWh), Russia (155 TWh), Norway (143 TWh), and India (116 TWh). China with 15.5 GW of new capacity to end the year with almost 229 GW of total installed hydropower capacity and 20.3 GW of pumped storage capacity, led the world for new capacity installed, followed by Turkey, Brazil, Vietnam, and Russia.

2.2.2.5 Biomass as alternative energy

However, compare to the other alternative energy resources, biomass benefits applicable in almost of the climate in different country make it has greater potential, since it is renewable, in contrast to the nature of the fossil fuels (Natarajan et al., 1998). Biomass is seen as one of the best options that can provide a renewable fuel which can be utilized in a range of energy conversion technologies and also has the added advantage of being CO_2 neutral (Farah, 2008). As all we know during photosynthesis, the process need carbon dioxide (CO_2) as a requirement and naturally the CO_2 cycle process could be obtain from biomass process make the surrounding ecosystem became more efficient. Energy from biomass can be produced from different processes, including thermochemical (direct combustion, gasification, and pyrolysis), biological (anaerobic digestion, fermentation), or chemical (esterification) technologies. Direct combustion can provide a direct near-term energy solution (Arias et al., 2008), but feedstock supply chain challenges must be overcome to implement such a solution on a large scale. Physical qualities inherent with raw biomass materials, such as low bulk density, high

moisture content, hydrophilic nature, and low calorific value, restrict the use of biomass for energy purposes (Arias et al., 2008). When compared to traditional fossil fuels, the low energy density values of biomass compounds these challenges. In addition, when large quantities of biomass are needed, problems associated with storage and transportation is subsequently created. Finally, grinding raw biomass with high moisture content is also challenging, as there is no specific equipment, which can increase costs, and in some cases, becomes highly impossible. All of these drawbacks have led to the development of some pre-processing techniques to make biomass more suitable for fuel applications Fact that fossil fuels cannot be renewable, limits in quantity and always increasing in cost due to world economic driving the demand for this alternative energy sources and made the industrial realized the potential of the woody biomass in the future.

According to International Energy Agencies (2012) the total primary energy from biomass supplied increased 2–3% in 2012 to reach approximately 55 EJ. The majority of biomass use is approximately 46 EJ which includes the heat produced from both modern and traditional biomass, animal waste, food crops and charcoal. The generation of electricity from traditional biomass contributed an estimated 6–7% of total global primary energy demand in 2012. At the same time for the total volume of modern biomass consumption contributed an estimated 3–4% of global primary energy in 2012, with an energy content of around 18.5 EJ. By the end of 2012, global bio-power capacity was approaching 83 GW, up 12% over compare to 2011. The electricity generated was around 350 TWh of worldwide in 2012, a 5% increase over the previous year. For the world biggest consumer and generator of bio-power, by calculation of generation outputs over the period 2010–2012, the United States lead followed by Germany and closely by Brazil and China, both of which are gaining ground rapidly.

2.3 Biomass Pretreatment

Lignocellulosic biomass is widely available, sustainable, and suitable for the researcher to study and develop the method to optimize its effeciency. However, in utilizing the various forms of lignocellulosic biomass there are many challenge need to be overcome. Then pretreatment is exist in order overcome the problem. To improve raw biomass materials, physical, chemical, biological, or thermal pretreatments may be used as the method. Considerations need to be taken when choosing a pretreatment are chemical

cost and environmental safety, energy requirements, time requirements, cost of reactor, and recovery of all components for further use. The pretreatment should be provide to access valuable biomass components, reduction of decomposition rate, and improvement of transportation and conversion abilities.

2.3.1 Thermal Pretreatment

Thermochemical biomass conversion technology represents the process of exposing organic material to elevated temperatures under an oxygen depleted atmosphere. The aim of such a process is to thermally break down lignocellulosic material into smaller compounds that can be utilized directly or more easily upgraded into value-added products. Burning biomass in an oxidative environment is the oldest conversion process practiced by man. Combustion, however, does not intend to produce value-added products in the form of fuels, chemicals or materials, as other thermochemical conversion technologies, but only heat energy (Basu, 2010).

Hydrothermal Carbonization (HTC), which is also known as wet torrefaction, is a pretreatment where biomass is immersed in liquid water under being heated to temperatures between 200 and 300 °C and inert atmosphere pressures which ensure that the water remains as liquid. HTC's products include a solid residue (biochar) of increased fuel value and a liquid solution of five carbon and six carbon sugars, along with acetic and other organic acids. Lynam(2011) states that additives to the basic process can enhance the higher heating value (HHV) of the biochar. By addition of acetic acid and/or Li chloride to the standard HTC process, when applied to loblolly pine at 230 °C, increases the HHV of the biochar up to 30% and removes cellulose from the raw biomass. Meanwhile, the addition of Ca lactate and Ca chloride to the HTC pretreatment at 260 °C of loblolly pine will enhances the reactions occurring so that the resulting biochar has increased HHV compared to that with no salt added. In addition, Lynam(2011) states that Ca salts can reduce SOx and NOx emissions from coal thermal conversion processes. If pretreated biomass with a Ca salt adhering to it is co-fired with coal, emissions may be ii reduced while less coal is needed. Adding Ca lactate, Li chloride, and Ca chloride to HTC pretreatment also will reduces the reaction pressure, enhancing process safety. Yan et al(2009) states that the characteristics of hydrothermal carbonization, including the shorter reaction time at lower temperature and reduced

equilibrium moisture content, which reduces degradation over time, indicate its greater feasibility for a seasonal feedstock .

The specificity of hydrothermal processing (HTP) that makes it different from other thermochemical conversion technologies is the liquid reaction environment. High air temperatures (250-350 °C and 4-17 MPa) or supercritical water temperatures (above 374 oC and 22 MPa) are usually utilized in this process. Under such conditions water serves as a solvent, reactant, and catalyst to assist in decomposition of lignocellulosic material into biocrude (similar to bio-oil) or gaseous products (similar to syngas), depending on temperature and pressure (Savage, 2010). The advantage of HTP is a relatively high efficiency for high moisture biomass conversion, which, however, comes at the expense of high capital and operating cost.

Pyrolysis is a thermochemical conversion of biological material into solid (char), liquid (pyrolysis/bio-oil), and permanents gases, under an inert atmosphere (Mohan et tal, 2006). Antal et tal (2003) states that pyrolysis has been used for producing charcoal for the past 38,000 years for a wide variety of uses, such as heating, cooking, art-making, metallurgy, chemical industry, purification, soil amelioration, and medicine. Fast pyrolysis has been developed relatively lately. It is different from traditional pyrolysis where charcoal is product of interest, mainly because it is aimed to produce liquid fuel that can be used as a substitute for crude oil. It utilizes high heating rates and short vapor reactor residence time. Bio-oil cannot be utilized directly in internal combustion engines and thus has to be upgraded in order to be used as a replacement for gasoline or diesel fuel (Antal et tal , 2003).

Gasification is a thermochemical conversion process where the primary goal is to produce a high yield of hydrogen and carbon monoxide, the gas mixture typically recognized as syngas. Mohan et al (2006) states that this process is different from pyrolysis, as it uses higher process temperatures and a partially oxidizing atmosphere. Gasification has been used for over 70 years to produce a low energy, density gas known as syngas (Huber et al, 2006) . Syngas can be converted into oxygenated fuels, hydrogen, alkanes by means of catalysts, and into a broad range of chemicals through intermediate products, such as methanol (Mohan et al, 2006).

Torrefaction also belongs to the group of thermochemical biomass upgrading technologies. This process is conducted in a temperature range of 200-300 °C, at atmospheric pressure, and under an inert atmosphere for duration of generally less than 1 hour.

2.3.2 Physical Pretreatment

Physical pretreatment involves breakdown of biomass size and crystallinity by milling or grinding. Improved hydrolysis results due to the reduction in crystallinity and improved mass transfer characteristics from reduction in particle size. The energy requirements for physical pretreatments are dependent on the final particle size and reduction in crystallinity of the lignocellulosic material. In most cases where a physical pretreatment is used, the required energy is higher than the theoretical energy content available in the biomass. This method is expensive and likely will not be used in a full-scale process.

Mechanical size reduction, to some degree, accompanies nearly all biomass pretreatment processes, and for that reason it is worth reviewing in more detail. Methods used to reduce biomass particle size include chipping, which results in a characteristic size of 10 mm to 30 mm, or grinding and milling, which result in a size ranging between 0.2 mm and 2.0 mm. The energy requirements of these processes are dependent on both the final dimension of the biomass and the source material. Both energy and power requirements increase rapidly as the particle size decreases, with 25% of the energy content of the biomass being consumed to achieve a particle size below 150 μm.

2.3.3 Biological Pretreatment

Biological pretreatment, as normally defined, involves the use of microorganisms (mainly fungi) to degrade lignin and hemicellulose but leave the cellulose intact (Kumar, 2009). Lignin degradation occurs through the action of lignin-degrading-enzymes secreted by the fungi. Even though biological pretreatments involve mild conditions and are of low cost, the disadvantages are the low rates of hydrolysis and long pretreatment times required compared to other technologies (Sun, 2002).

Kumar(2009) states that the current efforts in biological pretreatments are in combining this technology with other pretreatments and in developing novel microorganisms for rapidhydrolysis.

Thomass (2010) states that polysaccharide hydrolysis is hydrolysis follows the pretreatment step, with the goal of breaking down the cellulose and remaining hemicellulose to their constituent sugars, which will predominantly be comprised of glucose and xylose. This can be done either enzymatically or chemically. The enzymatic hydrolysis of cellulose to glucose is performed by a synergistic group of three separate enzymes, the cellulases endoglucanase and exoglucanase, and β-glucosidase. While all of these enzymes hydrolyze the β-1, 4 glycosidic bond, they each act on different regions of the cellulose polymer. Endoglucanases bind to the midsection of the polymer and cut internal glucosidic bonds along the polyglucan chain, releasing higher oligomers. Exoglucanases bind to the ends of the polyglucan chain, and its hydrolysis products are glucose and lower oligomers, primarily cellobiose. β-glucosidases hydrolyze cellobiose and water soluble cellodextrins with a degree of polymerization under six to glucose monomers. All three types of enzyme are necessary to efficiently break down cellulose to glucose.

Table 2-1: Different types of cellulolytic enzymes (Thomass, 2010)

Type	Bind to	Product
Endoglucanases	Mid Chain	Shorter chains
Exoglucanases	End of chain	Glucose Cellobiose Cellodextrins
β-glucosidases	Cellobiose/cellodextrins	Glucose

2.3.4 Chemical Pretreatment

Some of the existing physicochemical pretreatment strategies include dilute acid, steam explosion, liquid hot water (LHW), ammonia fiber expansion (AFEX), ammonia recycle percolation (ARP), and sodium hydroxide treatments. Several publications have come out over the last decade that has extensively reviewed many of these pretreatment